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Method for the production of a coated structure which is suitable for carrying out heterogeneous catalyses

The invention relates to a method in accordance with the preamble of claim 1, namely a method for the production of a coated structure which is suitable for carrying out heterogeneous catalyses. It also refers to corresponding catalyst bodies.

A catalyst body with a cross channel structure, of which the surfaces are coated which can be brought into contact with fluids, is known from EP-A 0 433 223 (= P. 6318). The cross channel structure has a construction which is formed of mutually bordering layers. Flow channels which are provided for the fluids, which are mutually open and which cross one another extend at boundary surfaces between adjacent layers. The coating of the catalyst body consists of a wash coat, which has a larger specific surface thanks to a high porosity. The wash coat serves as a carrier for catalytically active substances. In addition to the named catalyst body with cross channel structure, differently constructed catalyst bodies with coated surfaces are also known.

The object of the invention is to create a further method for the production of coated structures which are suitable as catalyst bodies

and the coatings of which advantageously have large specific surfaces. This object is satisfied by the method which is characterised in claim 1.

The method refers to the production of a coated structure which is suitable for carrying out heterogeneous catalyses. This structure is a catalyst body which comprises layers of film-like sheet metal lamina which are arranged one on the other and flow channels which are integrated in or between the layers. Some or all of the sheet metal lamina can be reshaped so that the flow channels arise as a result of a shaping of the sheet metal lamina. Coatings are applied in a container to the individual sheet metal lamina — preferably prior to a reshaping — with a plasma spray method, namely an LPPS method, using a plasma flame which acts defocusingly on an injected powder jet. These coatings contain catalytically active substances; they are porous or have a high roughness. A value between about 15 and 1500 Pa, preferably between 100 and 500 Pa, is set for the pressure in the container. After the coating and where appropriate a reshaping, the sheet metal lamina are fitted together to form a stack or a winding body.

Instead of sheet metal lamina in many cases tissues or other surface-like structures can be also used such as for example webs, fleeces or stretch grids. If in the following only sheet metal lamina are named in the description of the invention, then this is in each case to be understood such that as a rule other surface-like structures can as a totality or also selectively be substituted for the sheet metal lamina. In addition, for example tissues can also be formed into pockets, into which further catalyst material is contained in the form of fixed beds.

Catalyst bodies with a construction of this kind are known from EP-A 0 396 650 (= P.6216/47). Non-metals such as e.g. plastics, glass and/or carbon in the form of fibres are also possible as materials for the surface-like structures, with it being possible to combine different materials.

The method in accordance with the invention starts from a recent LPPS method (LPPS = Low Pressure Plasma Spraying), which is known from US-A 5 853 815 (E. Muehlberger). In this method a plasma flame is produced at a particularly low pressure. In comparison with older LPPS methods, a plasma flame arises which is widened when considered transversely and which acts defocusingly on a powder jet which is injected with a forwarding gas into the plasma. Within a duration which is short for thermal coating methods a large area can be brushed over with the plasma flame, which dispersely conveys the coating material. Uniform and very thin layers arise with an LPPS method of this kind, in which plasma flames for example up to 2.5 m in length are used. For the development of a coating with a high specific surface the coating must be built up with a large number of individual coats. Suitable coating material consists of aggregations of powder particles, for which the average particle diameter is preferably less than about 5 10^3 nm. Each particle, the diameter of which is not substantially smaller than the average diameter, is not or only partly melted in the plasma flame, so that a porous layer develops which has largely the microscopic structure of a powder pouring.

Subordinate claims 2 to 6 relate to advantageous embodiments of the method in accordance with the invention. The subject of claims 7 to 10 is a catalyst body with coatings which are produced in accordance with the LPPS method set forth in claim 1.

In the following the invention will be described with reference to the drawings. Shown are:

Fig. 1	a plant for the production of LPPS layers on sheet metal lamina,
Fig. 2	a drawing after an electron microscope image which represents a cross-section through an LPPS layer,
Fig. 3	a schematic illustration for a coating which contains individual large particles,
Fig. 4	a part of a catalyst body,
Fig. 5	section-wise, two layers of a cross channel structure and
Fig. 6	a stretch grid.

A plant 100, which is illustrated in a very simplified manner in Fig. 1 as an example, enables a continuous production of LPPS coatings 11 on a band-shaped sheet metal lamina 10 which can be transported through an evacuatable container 101 in the horizontal direction (arrow 111)

between an entry lock 110 (indicated in chain dotted lines) and an outlet lock 110'. With a spray gun 200 and by means of a broadened plasma flame 212 a coating material, which is present in the form of particles 12 of a powder P, is applied to the sheet metal lamina 10, with the flame 212 being moved back and forth transverse to the transport direction 111 by a pivoting of the gun 200. In this a central axis 2120 of the flame 212 makes a pendulum movement with its footprint on the surface of the sheet metal lamina band 10 between points of reversal 2121 and 2122. If as uniform a coating 11 as possible is desired, the points of reversal 2121 and 2122 must lie outside the band 10 — in contrast to the illustration of Fig. 1.

The gun 200, which is pivotal with a drive 210 and via a shaft 211, comprises a cathode 231 and an anode 232 with electrical connection lines 131 and 132 respectively. The electrodes 231 and 232 form a cavity in which a plasma is produced and a nozzle (not visible), via which the plasma flame 212 and the particles 12 which are carried along in it emerge.

A plant component 120 contains powder supplies as well as forwarding and metering devices for a powder P, which is used as coating material and which can be fed in via a flexible line 121 into the gun 200. Electrical energy E for the production of the plasma flame 212 is supplied via a current source 130 (current strength I) and the connection lines 132, 132 to the gun 200. A plant component 140 contains gas supplies and a metering and mixing device for a working gas G (mixture of argon, hydrogen, helium and/or nitrogen), which is

fed in via a line 141 into the gun 200. The low pressure which is required for the special LPPS method is produced with a further plant component 150. The sheet metal lamina 10 is drawn over a table 160 which can be designed as a cooler body (with corresponding, non-illustrated connections for the coolant).

The coating 11, which advantageously has a porous structure, is built up of the powder-like coating material through the application of a large number of individual coats. A coating thickness on the order of magnitude of 0.01 mm (= 10^4 nm) is provided for. The powder particles 12 of the coating material have an average diameter which is so large that each particle, the diameter of which is not substantially less than the average diameter, is only partly melted in the plasma flame; very large particles are not melted at all depending on the temperature of the plasma flame. One coat of dispersely distributed particles is applied per individual coating. The average thickness of the individual coat amounts to about 100 to 500 nm.

The sheet metal lamina 10 is, for example, sand blasted prior to the coating so that a surface results which leads to a good adhesion of the coating 11. By means of a roughness which is produced by the sand blasting — in relation to the catalytically active surfaces of the coating 11 — the specific surface, which should be large, can be advantageously influenced.

A ceramic material, for example Al_2O_3, can be used for the coating 11 in order to produce a carrier for a catalytically active substance, such as

for example platinum, palladium or other metals. During the coating a single coat or a plurality of individual coats of the carrier material are applied alternatingly with a single coat of the catalytically active substance. A simultaneous coat of carrier material and catalytically active substance is also possible. A catalytically active substance, for example Cu, can also be used for the coating material.

A result of the LPPS method is illustrated in Fig. 2 with reference to a drawing which is drawn after an electron microscopic preparation (thin grind, layer thickness about 30 μm). The powder particles 12, by means of which the coating 11 is built up on the substrate, namely the sheet metal lamina 10, with a thickness d, adhere to one another thanks to a partial melting, but produce a build-up which largely has the structure of a powder coating. A communicating inner space of pores 13 enables a diffusion of the reactants between the outer boundary of the coating 11 and the particle surfaces 12 contained in it.

For the production of the coating illustrated in Fig. 2 an Al_2O_3 powder was used, the particles of which have a size distribution which can be characterised by the following sieve analysis: -13 +2.0 μm (i.e. 5% of the particles are coarser than 13 μm and 2% finer than 2 μm). The substrate was water cooled. The process parameters were set as follows: powder infeed into the plasma flame 212 at 169 g/min and 48 SLPM (litres per minute, gas at normal conditions) forwarding gas; pressure in the container 101: 1100 Pa; argon infeed: 130 SLPM; distance between gun nozzle and substrate: 1.3 m; current strength I: 1000 A; number of individual coats: 300; relative speed between substrate 10 and plasma

flame 212: 138 m/min. The diameter of the plasma flame on the substrate amounts to about 0.4 m.

Through varying of the process parameters during the coating, gradients can be produced in the coating 11: a variable porosity (with porosities of practically 0% up to more than 10%) or a varying concentration of the catalytically active substance.

Materials for which a heterogeneous layer results can be used for the coating, namely such — see Fig. 3 — that the coating 11 is built up of a relatively small number of large particles 12' which are uniformly distributed in a homogeneous layer 11'. The homogeneous layer 11' is porous and is composed of a relatively large number of small particles. The large particles 12' preferably have a porous fine structure. The particles 12' produce a high roughness of the coating 11, which can lead to micro-turbulences in a flow of the fluid to be treated when sheet metal lamina 11 which are coated in such a manner are used in catalyst bodies. Micro-turbulences of this kind are advantageous, since they further a material transport through boundary layers of the fluid flow.

After the coating the sheet metal lamina 11 are brought into a suitable shape in which they can be fitted together to form a catalyst body 1. The coated sheet metal lamina 11 can — in planar form or after a reshaping — be wound to form a cylindrical body. In order to obtain flow channels for a fluid to be treated in a winding body of this kind, spacings must where appropriate be laid in between the coated sheet metal lamina 11.

The catalyst body 1 can also be formed as a stack of plane layers of sheet metal lamina 11 which are planar and smooth or are reshaped for the production of flow channels. Planar sheet metal lamina 11 are arranged at spacings so that flow channels remain free between them. For example every other one of the layers which are arranged one on the other can also consist of a reshaped sheet metal lamina 11 which forms flow channels.

The reshaped sheet metal lamina can be corrugated or have a zigzag-like cross-section. Fig. 4 shows section-wise a first example of a catalyst body 1 in accordance with the invention. The latter is alternatively fitted together of layers 2 with corrugated sheet metal lamina 10a, 10b and layers 3 with planar sheet metal lamina 10. The corrugated sheet metal lamina 10a are strips which extend transversely to the direction of a fluid flow 5, to the flow of the fluid to be treated. Adjacent strips 10a and 10b of the layer 2 are mutually displacedly arranged so that in each case new upstream edges 15 separate the fluid flow 5 into partial flows. Upstream edges 15 of this kind cause an improved material transport at the surfaces of the sheet metal lamina 10b through the influencing of the fluid flow. As a rule all sheet metal lamina 10, 10a and 10b are carriers of catalytic LPPS coatings.

The sheet metal lamina can have an additional fine structuring, for example a grooving (not illustrated). They can also contain apertures, for example in the form of circular holes, which are formed by removal — for example by punching out — of material.

Fig. 5 shows section-wise two adjacent layers 2 and 3 of a cross channel structure. In a catalyst body 1 with cross channel structure all sheet metal lamina are reshaped. The flow channels with fluid flows 5', 5" of adjacent layers 2, 3 are mutually open and cross one another.

All or some of the sheet metal lamina 10 can have apertures which are formed by means of regularly arranged slits and a reshaping. Sheet metal lamina 10 of this kind are for example stretch grids 4, see Fig. 6. The latter can also be used as coated or uncoated spacers between planar sheet metal lamina 10. Or stretch grids 4 of this kind which are coated can be reshaped to corrugated layers for a catalyst body 1 with cross channel structure.

The catalyst body in accordance with the invention can for example be used in exhaust gas catalysers. A further possible use is a reactive distillation in a column which contains a packing in the form of the catalyst body in accordance with the invention. In a column of this kind a) a material exchange between a trickle film on the packing surface and a gas which flows through the channels of the packing, and b) catalytic processes at the coated packing surfaces take place simultaneously.